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SPECTROSCOPIC STUDIES OF LASING TRANSITIONS IN THE DIATOMIC MER--ETC(U)
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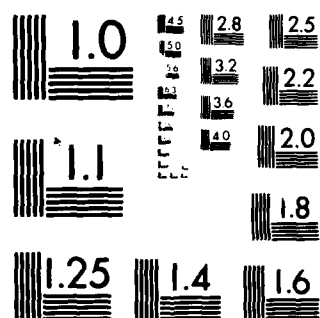
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SPECTROSCOPIC STUDIES OF LASING TRANSITIONS IN
THE DIATOMIC MERCURY HALIDES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission spectra of HgCl, HgBr, and HgI have been photographed and analyzed for the single isotopic species, $^{200}\text{Hg}^{35}\text{Cl}$, $^{200}\text{Hg}^{79}\text{Br}$, $^{200}\text{Hg}^{127}\text{I}$, and $^{200}\text{Hg}^{129}\text{I}$. In every case the vibrational analysis corroborates Wieland's earlier work [Helv. Phys. Acta 14, 420 (1941); Z. Elektrochem. 64, 761 (1960)] qualitatively but not quantitatively, in that the assignments deviate from his for high v'' levels, leading to lower estimates of the dissociation energies of the ground states. In addition the		

20

isotope effect for HgI indicates that Wieland's v'' numbering should be decreased by one unit. Trial-and-error Franck-Condon calculations yield the following values for $\Delta R_e (= R_e' - R_e'')$: 0.60 Å (HgCl), 0.57 Å (HgBr), and 0.49 Å (HgI). These values are somewhat larger than reported previously, and they lead to significant changes in the Franck-Condon distributions for HgCl and HgBr. Preliminary results of rotational analyses for HgCl and HgBr indicate that $R_e' \approx 3.00$ Å for HgCl and 3.056 Å for HgBr. Both values are only slightly larger than recent theoretical estimates.

The reported laser "lines" in all three molecules occur in the region of strongest spontaneous emission. However it seems that most of the laser features cannot be assigned to specific $v'-v''$ bands. Rather, they appear to occur on a quasicontinuum of densely overlapped rotational lines of several $v'-v''$ bands in the various isotopic HgX molecules present in "natural" HgX.

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Progress Summary

Our work in the first year of this contract has concentrated on the recording and analysis of $B \rightarrow X$ spectra for the single isotopic HgX species, $^{200}_{Hg}^{35}Cl$, $^{200}_{Hg}^{79}Br$, $^{200}_{Hg}^{127}I$, and $^{200}_{Hg}^{129}I$. In addition we have measured some features for $^{200}_{Hg}^{37}Cl$ and $^{200}_{Hg}^{81}Br$ using sources containing ^{200}Hg and natural Cl_2 or Br_2 . The preliminary vibrational analyses have been completed, and rotational analysis is currently underway for $HgCl$ and $HgBr$. A report of the work on $HgBr$ has been published (Appendix 1),¹ and a manuscript discussing the $HgCl$ and HgI work has been submitted (Appendix 2).²

In conjunction with the vibrational analyses for all three HgX molecules, we have calculated Franck-Condon factors in trial-and-error fashion to determine the relative configuration of the B and X potential curves. For $HgCl$ and $HgBr$ our FCFs are considerably different from those published by Cheung and Cool.³ In both cases the Franck-Condon distributions are shifted up in v'' by 2-3 units. These results are based on detailed comparisons of calculated FCFs and the observed intensity patterns for individual v' levels. The differences with results in Ref. 3 are due at least partly to differences in the X -state potential curves, as a consequence of our reanalysis. In particular, our constants extrapolate to values of the dissociation energy which are much lower than estimated by Wilcomb and Bernstein⁴ for all three molecules. Our preliminary FCFs for $HgBr$ and $HgCl$ are presented in Appendix 3. Although these values must be approximately correct, the reader is cautioned that the numbers will change as the analysis is extended and completed.

We have so far obtained only preliminary results from our rotational analyses of $HgCl$ and $HgBr$. These results indicate that $R_e' \approx 3.00 \text{ \AA}$ in $HgCl$ and 3.056 \AA in $HgBr$. Both values are only slightly larger than the theoretical estimates of Wadt.⁵ To date we have been able to analyze selected bands using a simple two-branch (P and R) model. However it is clear that four branches must occur (possibly overlapped), and three or four branches can be discerned in certain regions of the spectra. Thus the role of spin splitting in these systems is not yet clear.

For all three HgX molecules some of the previously reported laser "lines" can clearly be associated with prominent heads in the emission spectra. However most cannot, and it appears that lasing may be occurring on a near-continuum of overlapped rovibronic transitions in the several isotopic molecules of significance.

Future Work

We expect to complete the bulk of our work on the analyses for all three HgX molecules within three months. The results are intended to be published as three papers in the Journal of Molecular Spectroscopy. While we are completing this work, we will begin studies of the low-resolution overall intensity distributions as a function of pressure and temperature, in order to extract experimental estimates of the R-dependence of the B-X transition strength functions. At the same time we are beginning work on the pressure broadening of individual rotational lines in the HgCl and HgBr spectra, using the very high resolution capabilities of a Fabry-Perot interferometer. At a later date (~January, 1983) we expect to begin examining the transient B \leftarrow X absorption from low v' levels to high v' , using methods of kinetic spectroscopy in conjunction with either flash photolysis or our Tesla discharge as a source of ground-state HgX molecules.

The question of the specific assignment of the lasing transitions is not yet a closed issue, in my opinion. I am not convinced that existing measurements of the laser "lines" are precise enough for such specific assignment. While it may be true that lasing occurs on a quasi-continuum of overlapped lines, as I have suggested above, it should still be possible to identify precisely which overlapped transitions are involved. To this end very high resolution, precisely calibrated photographic spectra of the laser emissions are needed. We do not presently have the capability of performing the requisite experiments in my laboratory, but hope to be able to do so in the not too distant future.

References

1. J. Tellinghuisen and J. Gail Ashmore, Appl. Phys. Lett. 40, 867 (1982).
(See Appendix 1.)
2. J. Tellinghuisen, P. C. Tellinghuisen, S. A. Davies, P. Berwanger, and K. S. Viswanathan, Appl. Phys. Lett. (submitted). (See Appendix 2.)
3. N.-H. Cheung and T. A. Cool, J. Quant. Spectrosc. Radiat. Transfer 21, 397 (1979).
4. B. E. Wilcomb and R. B. Bernstein, J. Mol. Spectrosc. 62, 442 (1976).
5. W. R. Wadt, Appl. Phys. Lett. 34, 658 (1979).

Personnel

Two graduate students, K. S. Viswanathan and J. Gail Ashmore, have been employed essentially full time on this project. Mr. Viswanathan is completing his third year at Vanderbilt, and Miss Ashmore her second. A third graduate student, O. Carlisle Salter, has recently joined my group and is now also supported by this contract. Mr. Salter is a returning student who is roughly beginning his third year. Two undergraduate students have also been involved with this work: Patrick Berwanger was employed for three months in summer of 1981, and Sue A. Davies worked during the Spring, 1982 term in fulfillment of the laboratory requirement of her advanced general chemistry course. Finally, my wife Patricia C. Tellinghuisen has been employed one-fourth time since February, 1982, as Research Associate. She holds an M. Sc. degree in chemistry from the University of Canterbury (New Zealand).

Other Support

I presently have no other sources of funding. However, I will soon be requesting support from DARPA for work on the spectroscopy of XeF, and from the Air Force for work on halogen spectroscopy.

Publications

1. "The $B \rightarrow X$ transition in $^{200}_{79}\text{Hg Br}$," by Joel Tellinghuisen and J. Gail Ashmore, Appl. Phys. Lett. 40, 867 (1982). (Appendix 1)
2. "The $B \rightarrow X$ transitions in HgCl and HgI," by Joel Tellinghuisen, Patricia C. Tellinghuisen, Sue A. Davies, Patrick Berwanger, and K. S. Viswanathan, Appl. Phys. Lett. (submitted). (Appendix 2)

Appendix 1

The $B \rightarrow X$ transition in $^{200}\text{Hg } ^{79}\text{Br}$

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(Received 22 January 1982; accepted for publication 26 February 1982)

The $B \rightarrow X$ spectrum of HgBr is photographed and analyzed for the single isotopic species $^{200}\text{Hg } ^{79}\text{Br}$. The analysis confirms Wieland's earlier analysis [*Z. Elektrochem.* **64**, 761 (1960)] up to $v'' \approx 23$ but is different for higher v'' levels, leading to a lower estimate of the ground-state dissociation energy, $\mathcal{D}_0 = 5500 \text{ cm}^{-1}$. Franck-Condon calculations indicate that $R'_0 - R''_0 = 0.57 \text{ \AA}$, which is somewhat greater than concluded in earlier work. The previously reported HgBr laser lines appear not to coincide with specific band heads in the spectrum; instead they probably involve a semicontinuous overlap of rotational lines in several $v'-v''$ bands of the 12 isotopic HgBr molecules of significance in "natural" HgBr .

PACS numbers: 33.20.Kf, 33.10.Gx, 33.70. - w, 42.55.Hq

Although the mercury halide lasers are a subject of considerable current interest, surprisingly little spectroscopic work has been done on the lasing $B \rightarrow X$ transitions in the HgX molecules. The primary source of information on these systems is a series of papers published by Wieland over 20 years ago.¹⁻³ Most of Wieland's work involved emission sources prepared from "natural" HgX_2 , so his spectra included contributions from the large number of isotopic HgX molecules occurring in natural abundance. Similarly, most of the laser developmental research has utilized natural HgX_2 . In the latter work a number of problems of a spectroscopic nature have arisen, including the question of the specific identification of the lasing transitions.⁴ To help resolve these issues, we have begun a reanalysis of the $\text{HgX } B \rightarrow X$ transitions, using single-isotope emission sources. In this letter we present preliminary results of our vibrational analysis for $^{200}\text{Hg } ^{79}\text{Br}$.

Emission spectra were photographed using equipment and procedures similar to those employed previously in this laboratory in the study of halogen and rare-gas halide emission spectra.⁵⁻⁷ The sources consisted of 3-mm o.d. pyrex tubes about 10 cm long, which were charged initially with $^{200}\text{Hg } ^{79}\text{Br}_2$ (or $^{200}\text{HgBr}_2$ from natural Br_2) and ~ 200 Torr Ar, then sealed off with a torch. The ^{200}Hg (95.7% isotopic purity, Oak Ridge) was obtained in the form of HgO , which was decomposed *in situ* by heating under vacuum. The di-

bromide was then prepared by admitting $^{79}\text{Br}_2$ (98.6%, Oak Ridge, prepared from $\text{Na } ^{79}\text{Br}$ as described in Ref. 8) or natural Br_2 in excess and heating gently. The emission was excited with a teal coil,⁶ with the discharge tube heated to $\sim 135^\circ\text{C}$ to maintain a sufficient vapor pressure (~ 1 Torr) of HgBr_2 . Spectra were photographed on a 1.5-m JY spectrometer, using a 3600-groove/mm holographic grating (reciprocal dispersion $\sim 1 \text{ \AA/mm}$) and a 1200-groove/mm replica grating ($\sim 5 \text{ \AA/mm}$). Although rotational structure was clearly resolved with the former grating, the latter was actually better for discerning the band heads, which were measured with an estimated precision of 0.4 cm^{-1} .

Our interpretation of the spectrum agrees with Wieland's³ except at the long-wavelength end, where our assignments of bands having $v'' > 23$ differ from his. Below $v'' = 23$ our measurements lie consistently $2-4 \text{ cm}^{-1}$ below Wieland's, which is consistent with the small isotope shift for $^{200}\text{HgBr}$ vs $^{202}\text{HgBr}$. (Since ^{202}Hg is the most abundant Hg isotope and since for most of the assigned bands the blue-most feature is associated with the heaviest HgBr isomer, Wieland's measurements can, to a good approximation, be attributed to $^{202}\text{Hg } ^{79}\text{Br}$ and $^{202}\text{Hg } ^{81}\text{Br}$.) Above $v'' = 23$ our assignments deviate to the blue of Wieland's, with the disparity amounting to 20 cm^{-1} at $v'' = 28$ and 70 cm^{-1} at $v'' = 33$. In the region where these bands occur, the spectrum is quite congested; however, the progressions are

easy to follow up to $v'' = 31$ in our single-isotope spectrum, so we are confident of our assignments.

As a consequence of our reassignment of the high v'' bands, the dissociation energy of the ground state appears to be considerably smaller than Wieland's estimate of 5740 cm^{-1} and Wilcomb and Bernstein's⁹ value of 6000 cm^{-1} . The latter authors used long-range theory to extrapolate to dissociation. For our highest assigned level ($v'' = 34$) the absolute slope in the appropriate plot (see Fig. 2 in Ref. 9) is greater than the calculated limiting slope, which renders the extrapolation to dissociation uncertain. However, it appears unlikely that \mathcal{D}_0 can be greater than 5500 cm^{-1} and is more likely $\sim 5400 \text{ cm}^{-1}$. We are attempting to extend the assignments to higher v'' to refine this determination.

To date our assignments span v' levels 0–10 and v'' levels 11–34, and include 56 bands for $^{200}\text{Hg } ^{79}\text{Br}$ and 16 for $^{200}\text{Hg } ^{81}\text{Br}$ (measured in the spectrum of the $^{200}\text{HgBr}_2$ source). All assigned bands were least-squares fitted to the standard double polynomial expression⁵

$$\nu_i = T'_e + \sum_{j=1}^m c'_{ij} x_i'^j - \sum_{k=1}^n c''_{ik} x_i''^k, \quad (1)$$

where

$$x_i' = \rho(v_i' + 1/2), \quad x_i'' = \rho(v_i'' + 1/2), \quad (2)$$

and ρ is the isotopic factor ($\equiv 1.0000$ for $^{200}\text{Hg } ^{79}\text{Br}$, 0.991108 for $^{200}\text{Hg } ^{81}\text{Br}$). When the v'' numbering was altered by ± 1 from that given by Wieland, there were clear systematic deviations and a significant increase in the variance, from which we conclude that this numbering is correct. We obtained minimum variance with two upper and four lower-state vibrational parameters, given in Table I. These parameters represent the assigned bands with a standard deviation of 0.46 cm^{-1} and a maximum deviation of 1.2 cm^{-1} . Although the constants will change somewhat as we extend the assignments to lower and higher v'' , we expect them to remain valid to $\sim 0.5 \text{ cm}^{-1}$ in the calculation of the red-degraded band heads for the v' and v'' ranges spanned by our data.

Our vibrational analysis is corroborated by trial-and-error Franck-Condon calculations, in which we adjust the internuclear separation of the B and X states to match the calculated FCF's with the observed intensity patterns in the individual v'' progressions. In these calculations we have adopted Cheung and Cool's¹⁰ estimate of 2.62 Å for the internuclear distance of the ground state and have represented the X potential as a Morse-RKR curve, i.e., a Morse repulsive curve (determined from our estimated \mathcal{D}_e and ω_e values) and an attractive branch obtained by adding the RKR turning point differences,¹¹ $R_+(v) - R_-(v)$, to the repulsive branch at the appropriate energies. The B state was approximated as a Morse curve. Good agreement with the observed intensity distributions was obtained for $R'_e = 3.19 \text{ Å}$, which we estimate to be reliable within 0.01 Å, for our assumed lower curve shape and location. This value is 0.09 Å larger than obtained by Cheung and Cool.¹⁰ About 0.03 Å of this difference is due to a difference in the skewedness of the two X curves. (Our attractive branch lies about 0.03 Å to large R from that of Ref. 10 near $v = 20$ –21, where peak intensities

TABLE I. Spectroscopic parameters (cm^{-1}) for the B and X states of $^{200}\text{Hg } ^{79}\text{Br}$, valid for $v' = 0$ –10, $v'' = 11$ –34.^a

	$X(^2\Sigma^+)$	$B(^2\Sigma^+)$
T_e	0	23484.97
$c_{e1}(\omega_e)$	188.249	135.887
$c_{e2}(-\omega_e x_e)$	-1.0359	-0.2527
c_{e3}	-1.5068×10^{-3}	
c_{e4}	-2.4809×10^{-4}	
\mathcal{D}_e	5500	39100 ^b
$c_{v1}(B_e)$	0.04345	0.02928
$c_{v2}(-\alpha_e)$	-3.274×10^{-4}	-7.3×10^{-5}
c_{v3}	5.973×10^{-6}	
c_{v4}	-2.351×10^{-7}	
$R_e(A)$	2.62	3.19

^aAll rotational constants are based on assumptions about potentials; see text.

^bAssuming dissociation to $\text{Hg}(^1S) + \text{Br}(^1S)$. The lowest $\text{Hg}^* + \text{Br}$ asymptote lies 19400 cm^{-1} lower.

occur in the $v' = 0$ progression.) However, the remaining 0.06 Å is significant, and it serves to shift the Franck-Condon pattern of Table 10 in Ref. 10 up by 3 quanta in v'' . (For example, the observed Franck-Condon "gap" for $v' = 1$ in our spectrum occurs near $v'' = 20$ –21 instead of $v'' = 17$ –18 as indicated in Table 10 of Ref. 10.) We hope to refine the X curve shape and pin down the absolute R_e values through a rotational analysis. The Franck-Condon factors will be published when the full analysis is completed.¹²

For the X potential used in the FCF calculations, we have calculated rotational constants and fitted them to the standard expression,

$$B_v = \rho^2 \sum_{i=1}^L c_{vi} x_i'^{-1}, \quad (3)$$

where ρ and x are as defined previously. The resulting constants are included in Table I, together with the Morse B_e and α_e values for the B state. We emphasize that these values can only be taken as a rough approximation of the true values, as they are grounded entirely on our assumptions about the X curve and our FCF calculations; consequently they will certainly change when the rotational analysis is completed. However, several points are worth noting: (1) The two-parameter expression for B_v assumed in Ref. 10 is inadequate to represent the B_v values for levels as high as $v'' = 20$. (2) Our B_v values are lower than those in Table 3 of Ref. 10 by 4% at $v = 20$ and 9% at $v = 30$. (3) The constants predict that all low v' bands will be simple red degraded (i.e., $B_v'' > B_v'$; up to $v'' \approx 33$; for larger v'' , spikes and violet-degraded bands should occur, as they do in other emission spectra of this type.^{5,8} The last result is in fact borne out in the observed spectra.

Lasing has been reported near 5018 and 4996 Å by Parks,¹³ and in two three-peak groups near 5020 and 5040 Å by Schimitschek and coworkers.^{14,15} The latter group has obtained more precise measurements of these six peaks,¹⁶ which are compared with calculated band heads in this spectral region for all 12 HgBr isotopomers in Table II. While there are a few coincidences, the bands involved are not particularly strong, so it appears that lasing does not occur pre-

TABLE II. Calculated wave numbers (cm^{-1}) of $\text{HgBr } B \rightarrow X$ band heads near measured laser lines at 19817.3, 19833.0, 19844.0, 19896.1, 19906.0, and 19916.4 cm^{-1} .^{a,b}

Species	Abundance (%)	ρ	Band ($\nu'-\nu''$)								
			0-23	5-29	1-24	2-25	3-26	4-27	0-22	1-23	2-24
198, 79	5.1	1.001429	19792.2	19796.4	19805.6	19822.5	19843.2	19867.8	19918.4	19927.8	19940.6
199, 79	8.5	1.000711	794.3	797.9	807.5	824.4	845.0	869.4	920.4	929.7	942.5
200, 79	11.7	1.000000	796.3	799.4	809.5	826.2	846.7	871.1	922.4	931.7	944.4
201, 79	6.7	0.999294	798.3	800.9	811.4	828.1	848.5	872.8	924.4	933.6	946.2
202, 79	15.1	0.998596	800.3	802.4	813.3	829.9	850.2	874.4	926.4	935.5	948.0
204, 79	3.5	0.997218	804.2	805.4	817.1	833.5	853.7	877.7	930.2	939.2	951.6
198, 81	4.9	0.992551	817.6	815.6	830.0	845.8	865.4	888.7	943.4	952.0	963.8
199, 81	8.3	0.991825	819.7	817.2	832.0	847.8	867.2	890.4	945.5	954.0	965.8
200, 81	11.4	0.991108	821.7	818.7	834.0	849.7	869.0	892.1	947.5	955.9	967.6
201, 81	6.5	0.990396	823.8	820.3	835.9	851.5	870.8	893.8	949.5	957.8	969.5
202, 81	14.7	0.989692	825.8	821.8	837.9	853.4	872.6	895.5	951.5	959.8	971.4
204, 81	3.4	0.988301	829.8	824.9	841.7	857.1	876.1	898.8	955.5	963.6	975.0

^aMeasurements from Ref. 16.

^bIncludes all bands having $\nu' < 6$ which are prominent in our $^{200}\text{Hg } ^{79}\text{Br}$ spectrum.

entially near any specific band heads. Rather it is likely that lasing is occurring on a nearly continuous overlap of rotational lines in the many overlapped $\nu'-\nu''$ bands of the 12 isotopomers.¹⁷ It should be noted that this overlap is so extensive that most of the calculated band heads in Table II cannot possibly be discerned in the spectrum of "natural" HgBr and can only be accounted for though the analysis of a single-isotopic species.

We thank Erhard Schimitschek for arousing our interest in this project, and Frank Hanson for communicating to us the laser wavelengths of Table II. This work was supported by the Office of Naval Research.

¹K. Wieland, *Helv. Phys. Acta* 2, 46 (1929).

²K. Wieland, *Helv. Phys. Acta* 14, 420 (1941).

³K. Wieland, *Z. Elektrochem.* 64, 761 (1960).

⁴E. J. Schimitschek (private communication).

⁵J. Tellinghuisen, *Chem. Phys. Lett.* 49, 485 (1977).

⁶M. R. McKeever, A. Sur, A. K. Hui, and J. Tellinghuisen, *Rev. Sci. Instrum.* 50, 1136 (1979).

⁷A. Sur, A. K. Hui, and J. Tellinghuisen, *J. Mol. Spectrosc.* 74, 465 (1979).

⁸A. Sur and J. Tellinghuisen, *J. Mol. Spectrosc.* 88, 323 (1981).

⁹B. E. Wilcomb and R. B. Bernstein, *J. Mol. Spectrosc.* 62, 442 (1976).

¹⁰N.-H. Cheung and T. A. Cool, *J. Quant. Spectrosc. Radiat. Transfer* 21, 397 (1979).

¹¹J. Tellinghuisen, *J. Mol. Spectrosc.* 44, 194 (1972).

¹²J. G. Ashmore and J. Tellinghuisen (unpublished).

¹³J. H. Parks, *Appl. Phys. Lett.* 31, 297 (1977).

¹⁴E. J. Schimitschek, J. E. Celto, and J. A. Trias, *Appl. Phys. Lett.* 31, 608 (1977).

¹⁵E. J. Schimitschek and J. E. Celto, *Opt. Lett.* 2, 64 (1978).

¹⁶F. Hanson, T. Shay, and E. J. Schimitschek (unpublished).

¹⁷At 400 K the most populous rotational levels in the B state have $J' \approx 65$. The R and P lines in this J' region are the strongest individual lines in a given band. The rotational constants in Table I predict these lines to lie about 30 cm^{-1} to the red of the band head.

Appendix 2 (Submitted to Applied Physics Letters)

The B \rightarrow X transitions in HgCl and HgI

by

Joel Tellinghuisen, Patricia C. Tellinghuisen, Sue A. Davies

Patrick Berwanger, and K. S. Viswanathan

Department of Chemistry

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Abstract

The B \rightarrow X spectra of HgCl and HgI are studied at high resolution for the single isotopic species, $^{200}\text{Hg}^{35}\text{Cl}$, $^{200}\text{Hg}^{127}\text{I}$, and $^{200}\text{Hg}^{129}\text{I}$. For HgI the analysis indicates that the v'' numbering should be decreased by one unit from the previous assignment. For both molecules the analyses deviate progressively from the previous assignments at high v'' , extrapolating to lower estimates of the ground state dissociation energies. Franck-Condon calculations yield $\Delta R_e (= R_e' - R_e'')$ = 0.60 Å for HgCl and 0.49 Å for HgI. The strongest laser features previously reported for HgCl occur near the heads of the overlapped 0-22, 1-23, 2-24, and 3-25 bands. The HgI laser operates in the region of the 0-14, 0-15, 1-15, 1-16, 2-17, and 2-18 bands.

In the search for new, high-power, UV-visible lasers, considerable attention has been focused on the B-X transitions in the diatomic mercury halides. To refine the spectroscopic characterization of these systems, we have been studying the emission spectra of isotopically pure HgX molecules. We reported recently preliminary results of our work on HgBr.¹ In this paper we discuss the results of our vibrational analyses for HgCl and HgI.

The emission spectra were obtained using equipment and procedures similar to those described previously.¹⁻⁴ The Tesla discharge sources were charged initially with the desired isotopic HgX species, which were prepared *in situ* as described for HgBr.¹ Most of the work involved sources containing $^{200}\text{Hg}^{35}\text{Cl}$ and $^{200}\text{Hg}^{127}\text{I}$. To determine the vibrational numbering we also photographed and measured spectra of $^{200}\text{Hg}^{129}\text{I}$ ($^{129}\text{I}_2$ from Oak Ridge, stated isotopic purity 99%), and $^{200}\text{Hg}^{37}\text{Cl}$ (from a source made with natural Cl_2). HgCl spectra were photographed over the region 4400-5800 Å, at a reciprocal dispersion of ~ 5.3 Å/mm. The HgI spectra were recorded for the region 4050-4500 Å; most of the assignments were from plates having a reciprocal dispersion of ~ 1.1 Å/mm, with a few obtained from plates exposed at the lower resolution employed for HgCl.

As in the case of our earlier work on HgBr, our interpretation of the spectra of both molecules agrees qualitatively with Wieland's^{5,6} previous work, except at the long-wavelength end. However, our least-squares analysis (see below) indicates that the v'' numbering suggested by Wieland for HgI should be decreased by one unit. (Wieland's numbering was stated to be uncertain for lack of a halogen isotope effect, since natural I_2 is 100% $^{127}\text{I}_2$.) Below $v'' = 14$ in HgI and $v'' = 20$ in HgCl, our measurements lie uniformly 2-3 cm^{-1} below Wieland's, which is consistent with the small isotope shift for ^{200}HgX vs the ^{202}HgX which dominated Wieland's spectra. However, for higher v'' our assignments deviate progressively to the blue of Wieland's, with the discrepancy

amounting to 30 cm^{-1} for our highest presently assigned levels ($v'' = 23$) in HgI, and about 40 cm^{-1} in HgCl ($v'' = 31$). As for HgBr, the relevant bands lie in very congested regions of the spectra and are likely blended to indistinction in spectra of "natural" HgCl and HgI. The assignments can be made with confidence in our single species spectra.

At present our assignments for $^{200}\text{Hg}^{35}\text{Cl}$ include 39 bands spanning v' levels 0-9 and v'' levels 11-31. For HgI we have assigned 50 bands for $^{200}\text{Hg}^{127}\text{I}$ and 54 for $^{200}\text{Hg}^{129}\text{I}$, spanning $v' = 0-13$ and $v'' = 5-23$. The assignments can be extended provisionally to higher v'' in both cases; however, the bands in question display anomalous profiles, requiring care in the estimation of band origins from the measured heads. Consequently we are continuing to work on these regions. The assigned bands have been least-squares fitted to the standard double polynomials in $\rho(v'+1/2)$ and $\rho(v''+1/2)$ (see Eqs. 1 and 2 in ref. 1). For HgI the variance increases by a factor of two when the v'' numbering is altered by ± 1 from our new numbering (which is reduced by one unit from Wieland's), so the new numbering is preferred. For HgCl we have fitted only the bands measured for $^{200}\text{Hg}^{35}\text{Cl}$. However, we have verified Wieland's numbering by measuring several prominent bands in the $v' = 0$ progression for $^{200}\text{Hg}^{37}\text{Cl}$. In this case the effect of the change in the Cl mass is substantial, so that a change in the v'' numbering represents a $\sim 5 \text{ cm}^{-1}$ shift in the band positions. The agreement is within 1 cm^{-1} , in confirmation of Wieland's numbering.

Minimum variance was achieved in the least-squares fits using 2 upper state parameters and 4 lower state parameters for both molecules. The results are presented in Table I. The reader is cautioned not to trust these constants outside the v' and v'' regions spanned by the assignments. For example the minimum of the X state remains uncertain by about 20 cm^{-1} in HgCl, relative to the lowest assigned v'' level. However, within the sampled regions these

constants should permit calculation of band positions reliable to about the standard deviations in the fits (0.37 cm^{-1} for HgCl, 0.19 cm^{-1} for HgI). This reliability should extend to the other isotopic molecules, for which band positions can be calculated by substituting the appropriate isotopic ρ values in the polynomials. These ρ values are summarized in Table II. For reference we note that the isotopic shifts in the region of strong emission are about 1.1 cm^{-1} per unit Hg mass change for HgI, and about 1.5 cm^{-1} for HgCl.

We have attempted to estimate the dissociation energies for the X states of both molecules using long-range theory in the manner employed by Wilcomb and Bernstein.⁷ However, in both cases we have encountered the same problem met in the work on HgBr: For our highest assigned levels the absolute slopes in the appropriate long-range plots are already greater than the theoretical limiting slopes. Consequently we can presently give only rough upper bounds on D_0 of 2850 cm^{-1} and 8200 cm^{-1} for HgI and HgCl, respectively. These values are $300\text{--}400 \text{ cm}^{-1}$ lower than estimated by Wilcomb and Bernstein and in fact are close to the original estimates of Wieland.

Frank-Condon calculations corroborate our vibrational assignments and indicate that R_e' is larger than R_e'' by 0.60 \AA in HgCl and 0.49 \AA in HgI. In these calculations we took the approach used in the work on HgBr: We fixed the X curves at the R_e values used by Cheung and Cool,⁸ and varied the internuclear distance in the B states. The X curves were approximated as Morse/RKR curves,⁹ and the B curves as Morse curves. The resulting R_e' values are thought to be reliable within 0.01 \AA , relative to the X curves in the region for strong emission. For HgI our R_e' value is 0.03 \AA larger than Cheung and Cool's. However this difference is entirely due to a shift in the attractive branch of the X curve in the Frank-Condon region of strong emission; and with the change in the v'' numbering, our Frank-Condon distributions are in agreement with

theirs. For HgCl our R_e' value is 0.08 \AA larger than Cheung and Cool's. Most of this difference is significant, and it results in a shift of the Frank-Condon distributions upward by two v'' units (e.g., the FC gap for $v' = 1$ occurs near $v'' = 19$ instead of $v'' = 17$, as indicated in Table 8 of ref. 8).

The R_e values are known in only a relative sense, as we have not yet analyzed rotational structure. However, preliminary examination of several strong bands in the $v' = 0$ progression for HgCl indicates that R_e' is $\sim 3.00 \text{ \AA}$ in this molecule. This value is slightly smaller than the value in Table I but larger than Wadt's¹⁰ theoretical estimate (2.93 \AA). For HgBr the experimental estimate¹¹ is 3.06 \AA , which is only 0.02 \AA larger than the theoretical value.¹⁰ Although the rotational constants for HgI and HgCl have not yet been determined experimentally, we include as guidelines in Table I the parameters calculated for the X curves employed in the Frank-Condon calculations.

Lasing has been reported for HgI at a number of wavelengths between 1414 \AA and 4450 \AA ,¹²⁻¹⁴ and for HgCl in the $5334\text{--}5658 \text{ \AA}$ region.^{12,14-17} The laser features generally correspond to the most intense features in the spontaneous emission spectra and probably involve multiply overlapped rovibronic transitions in the several isotopic molecules of significance (see Table II). The prominent $v'-v''$ bands in the lasing region for HgI are 0-13, 0-14, 1-15, 1-16, 2-17, 2-18, 3-18, 3-19, 4-19, 4-20, 5-21, and 5-23. The strongest features in the HgCl laser spectrum occur near 5580 \AA and undoubtedly involve appreciable contributions from transitions in the nearly coincident 0-22 and 1-23 bands, as has been noted previously. The 2-24 and 3-25 bands could also contribute significantly, as they lie very close to the other two and have large FCfs.

In a recent paper Kvasnik and King¹⁷ have measured and assigned 41 features in the HgCl laser spectrum. While many of the listed features likely involve some of the indicated bands, we think it is unwise to make specific $v'-v''$

assignments for most of these lines, as they probably involve circumstantial overlap of rotational lines in several bands of the various isotopic molecules. Furthermore, Kvasnik and King's high- v'' assignments are inconsistent with our reanalysis of this transition. These authors also concluded that the HgCl emission in the 5540-5730 Å region includes a significant broadband contribution, attributed to a bound-free transition. We think it unlikely that such a bound-free transition could involve any of the known states of HgCl for the following reasons: (1) The B-X transition should lie about 4000 cm^{-1} to the red of B-X. (2) The C-A and D-A systems may occur in this region; however, if these systems are present, the C-X and D-X systems should occur strongly in the UV. To our knowledge strong emission in the latter systems has not been reported for typical laser excitation conditions. (3) The continuum of the B-X transition falls precisely in this region; however the Franck-Condon properties of this system prohibit significant continuous emission from v' levels < 11 . At a typical operating temperature of 150°C the Boltzmann factor for the sum of all levels > 10 is about 10^{-3} . Thus if vibrational thermalization is appreciable, the B-X continuum must be negligible. While we cannot rule out broadband emission from other species in Kvasnik and King's laser system, we think it possible that their continuum is simply the quasicontinuum of densely overlapped lines in the B-X discrete emission. Even in our high-resolution, single-isotope spectra the emission appears almost continuous in some regions.

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References

1. J. Tellinghuisen and J. G. Ashmore, Appl. Phys. Lett. **40**, 867 (1982).
2. J. Tellinghuisen, Chem. Phys. Lett. **49**, 485 (1977).
3. M. R. McKeever, A. Sur, A. K. Hud, and J. Tellinghuisen, Rev. Sci. Instrum. **50**, 1136 (1979).
4. A. Sur, A. K. Hud, and J. Tellinghuisen, J. Mol. Spectrosc. **74**, 465 (1979).
5. K. Wieland, Helv. Phys. Acta **14**, 420 (1941).
6. K. Wieland, Z. Elektrochem. **64**, 761 (1960).
7. B. E. Wilcomb and R. B. Bernstein, J. Mol. Spectrosc. **62**, 442 (1976).
8. N.-H. Cheung and T. A. Cool, J. Quant. Spectrosc. Radiat. Transfer **21**, 397 (1979).
9. S. D. Henderson and J. Tellinghuisen, to be published.
10. W. R. Vadt, Appl. Phys. Lett. **34**, 658 (1979).
11. J. G. Ashmore and J. Tellinghuisen, J. Mol. Spectrosc., to be published.
12. E. J. Schimitschek, J. E. Celto, and F. Hanson, unpublished work.
13. Yu. E. Gavrilova, V. S. Zrodnikov, A. D. Klementov, and A. S. Podsonov, Sov. J. Quantum Electron. **10**, 1457 (1980).
14. R. Burnham, Appl. Phys. Lett. **33**, 156 (1978).
15. J. H. Parks, Appl. Phys. Lett. **31**, 192 (1977).
16. K. Y. Tang, R. O. Hunter, Jr., J. Oldenettel, C. Horton, D. Rustia, D. Eckstrom, B. Perry, and M. McCusker, Appl. Phys. Lett. **32**, 226 (1978).
17. P. Kvasnik and T. A. King, Optics Commun. **41**, 199 (1982).

TABLE II. Isotopic factors and abundances for isotopic species in HgCl and HgI.^a

HgCl	Abundance	ρ	HgI	Abundance	f
198,35	7.6%	1.000752	198,127	10.0%	1.001961
199,35	12.7	1.000374	199,127	16.8	1.000975
200,35	17.4	1.000000	200,127	23.1	1.000000
201,35	10.0	0.999629	201,127	13.2	0.999032
202,35	22.5	0.999262	202,127	29.8	0.998074
204,35	5.2	0.998538	204,127	6.9	0.996181
198,37	2.4	0.977508			
199,37	4.1	0.977121			
200,37	5.7	0.976738			
201,37	3.2	0.976358			
202,37	7.3	0.975982			
204,37	1.7	0.975241			

Reference molecules are $^{200}\text{Hg}^{35}\text{Cl}$ and $^{200}\text{Hg}^{127}\text{I}$.TABLE I. Spectroscopic parameters (cm^{-1}) for the B-X transitions in HgCl and HgI.^a

	$^{200}\text{Hg}^{35}\text{Cl}^b$	$^{200}\text{Hg}^{127}\text{I}^c$
T_e	23451.6	24066.4
$\nu_1'(\omega_e')$	191.941	110.850
$\nu_2'(-\omega_e'x_e')$	-0.4754	-0.1716
$\nu_1''(\omega_e'')$	298.973	123.053
$\nu_2''(-\omega_e''x_e'')$	-2.1513	-0.7130
ν_3''	1.0112×10^{-2}	-3.1161×10^{-2}
ν_4''	-5.0562×10^{-4}	2.7567×10^{-4}
r_e	0.37	0.19
D_e'	39900 ^d	38300 ^d
D_e''	8350	2900
$R_e'(\text{\AA})$	3.02	3.30
$R_e''(\text{\AA})$	2.42	2.81
$\nu_{r1}'(\theta_e')$	0.06210	0.01994
$\nu_{r2}'(-\omega_e')$	-9.1×10^{-4}	-4.2×10^{-5}
$\nu_{r1}''(\theta_e'')$	0.09674	0.02747
$\nu_{r2}''(-\omega_e'')$	-7.239×10^{-4}	-1.954×10^{-4}
ν_{r3}''	9.006×10^{-6}	-6.466×10^{-7}
ν_{r4}''	-4.889×10^{-7}	-1.571×10^{-7}

^aAll rotational constants are intended as guidelines only, as they are based upon assumptions about the potential curves; see text.^bVibrational constants valid for $v'=0-9$, $v''=11-31$.^cVibrational constants valid for $v'=0-13$, $v''=5-23$.^dAssuming dissociation to $\text{Hg}^*(^3\text{S}) + \text{X}(^1\text{S})$. The lowest $\text{Hg}^* + \text{X}$ asymptote lies $1-100 \text{ cm}^{-1}$ lower in HgCl and 21800 cm^{-1} lower in HgI.

Appendix 3a: Preliminary FCFs for $^{200}\text{Hg}^{35}\text{Cl}$, $v' = 0-5$, $v'' = 9-32$.

FRANCK-CONDON FACTORS, R-CENTROIDS, AND R=2-CENTROIDS

INTEGRALS TAKEN OVER 221 POINTS, STARTING AT $I = 1$ FOR STATE 1 AND $I = 141$ FOR STATE 2

FRANCK-CONDON FACTORS

V_0	$V_{00} = 9$	$V_{00} = 10$	$V_{00} = 11$	$V_{00} = 12$
0	1.4140E-01	7.3995E-01	3.3088E-04	1.2691E-01
1	1.4243E-04	6.4309E-04	2.4334E-03	7.7050E-03
2	7.2909E-04	2.8238E-03	8.9563E-03	2.3047E-02
3	2.5187E-02	8.3000E-01	2.1772E-02	4.4465E-02
4	6.5764E-03	1.8241E-02	3.8804E-02	6.0598E-02
5	1.3770E-02	3.1464E-02	5.3078E-02	5.9496E-02

R-CENTROID VALUES (ANGSTROMS)

V_0	$V_{00} = 9$	$V_{00} = 10$	$V_{00} = 11$	$V_{00} = 12$
0	2.8360E+00	2.8505E+00	2.8656E+00	2.8812E+00
1	2.8251E+00	2.8391E+00	2.8535E+00	2.8683E+00
2	2.8147E+00	2.8281E+00	2.8419E+00	2.8560E+00
3	2.8046E+00	2.8176E+00	2.8308E+00	2.8442E+00
4	2.7949E+00	2.8074E+00	2.8201E+00	2.8329E+00
5	2.7855E+00	2.7976E+00	2.8097E+00	2.8219E+00

R=2-CENTROIDS

V_0	$V_{00} = 9$	$V_{00} = 10$	$V_{00} = 11$	$V_{00} = 12$
0	8.0450E+00	8.1278E+00	8.2136E+00	8.3030E+00
1	7.9832E+00	8.0623E+00	8.1440E+00	8.2289E+00
2	7.9240E+00	7.9998E+00	8.0777E+00	8.1579E+00
3	7.8672E+00	7.9400E+00	8.0144E+00	8.0905E+00
4	7.8126E+00	7.8825E+00	7.9537E+00	8.0257E+00
5	7.7599E+00	7.8272E+00	7.8951E+00	7.9628E+00

FRANCK-CONDON FACTORS

V_0	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$	$V_{00} = 16$
0	4.1830E-03	1.1843E-02	2.8738E-02	5.9493E-02
1	2.0294E-02	4.3934E-02	7.6509E-02	1.0308E-01
2	4.7225E-02	7.4432E-02	8.4285E-02	5.8395E-02
3	6.7783E-02	7.0884E-02	4.0208E-02	3.8583E-03
4	6.3326E-02	3.4594E-02	2.3739E-03	1.3069E-02
5	3.5615E-02	3.6294E-03	9.7461E-03	4.1255E-02

R-CENTROID VALUES (ANGSTROMS)

V_0	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$	$V_{00} = 16$
0	2.8973E+00	2.9142E+00	2.9319E+00	2.9505E+00
1	2.8835E+00	2.8993E+00	2.9156E+00	2.9324E+00
2	2.8704E+00	2.8852E+00	2.9001E+00	2.9144E+00
3	2.8579E+00	2.8715E+00	2.8842E+00	2.8860E+00
4	2.8457E+00	2.8575E+00	2.8570E+00	2.8478E+00
5	2.8333E+00	2.8372E+00	2.8707E+00	2.8789E+00

R=2-CENTROIDS

V_0	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$	$V_{00} = 16$
0	8.3964E+00	8.4943E+00	8.5976E+00	8.7071E+00
1	8.3162E+00	8.4071E+00	8.5014E+00	8.5992E+00
2	8.2403E+00	8.3247E+00	8.4102E+00	8.4927E+00
3	8.1678E+00	8.2452E+00	8.3172E+00	8.3701E+00
4	8.0975E+00	8.1639E+00	8.1521E+00	8.4010E+00
5	8.0264E+00	8.0422E+00	8.2453E+00	8.2887E+00

FRANCK-CONDON FACTORS

V ₀	V ₀₀ = 17	V ₀₀ = 18	V ₀₀ = 19	V ₀₀ = 20
0	1.0433E-01	1.5338E-01	1.8631E-01	1.8320E-01
1	9.9345E-02	5.6032E-02	6.9997E-03	1.3199E-02
2	1.3517E-02	3.6404E-03	4.9227E-02	8.0533E-02
3	1.1733E-02	5.2955E-02	4.9426E-02	4.4489E-03
4	4.7970E-02	3.4613E-02	3.6162E-04	2.9475E-02
5	3.0458E-02	2.0361E-04	2.6602E-02	3.9417E-02

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 17	V ₀₀ = 18	V ₀₀ = 19	V ₀₀ = 20
0	2.9703E+00	2.9916E+00	3.0146E+00	3.0399E+00
1	2.9494E+00	2.9653E+00	2.9647E+00	3.0431E+00
2	2.9237E+00	2.9803E+00	2.9785E+00	2.9931E+00
3	2.9303E+00	2.9392E+00	2.9515E+00	2.9413E+00
4	2.9070E+00	2.9177E+00	2.8516E+00	2.9646E+00
5	2.8889E+00	2.8174E+00	2.9298E+00	2.9378E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 17	V ₀₀ = 18	V ₀₀ = 19	V ₀₀ = 20
0	8.8241E+00	8.9502E+00	9.0881E+00	9.2412E+00
1	8.6984E+00	8.7907E+00	8.7782E+00	9.2692E+00
2	8.5428E+00	8.8933E+00	8.8735E+00	8.9580E+00
3	8.5915E+00	8.6401E+00	8.7096E+00	8.6365E+00
4	8.4513E+00	8.5109E+00	8.0832E+00	8.7917E+00
5	8.3440E+00	7.8837E+00	8.5861E+00	8.6290E+00

FRANCK-CONDON FACTORS

V ₀	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23	V ₀₀ = 24
0	1.4163E-01	8.2366E-02	3.3549E-02	8.3886E-03
1	9.1165E-02	1.7169E-01	1.7233E-01	1.0026E-01
2	3.6493E-02	1.2098E-03	8.3389E-02	1.9204E-01
3	2.2615E-02	7.2769E-02	2.9175E-02	1.2883E-02
4	5.0524E-02	4.6078E-03	2.9421E-02	4.3016E-02
5	1.4718E-03	2.9700E-02	3.9501E-02	3.4232E-04

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23	V ₀₀ = 24
0	3.0686E+00	3.1022E+00	3.1442E+00	3.2033E+00
1	3.0531E+00	3.0786E+00	3.1111E+00	3.1532E+00
2	3.0024E+00	3.2021E+00	3.0971E+00	3.1228E+00
3	3.0109E+00	3.0177E+00	3.0138E+00	3.1846E+00
4	2.9730E+00	2.9541E+00	3.0332E+00	3.0310E+00
5	2.9044E+00	2.9856E+00	2.9890E+00	3.2156E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23	V ₀₀ = 24
0	9.4157E+00	9.6221E+00	9.8821E+00	1.0252E+01
1	9.3249E+00	9.6790E+00	9.6786E+00	9.9399E+00
2	9.0091E+00	1.0279E+01	9.5980E+00	9.7843E+00
3	9.0709E+00	9.1060E+00	9.0714E+00	1.0031E+01
4	8.8375E+00	8.7091E+00	9.2080E+00	9.1825E+00
5	8.4088E+00	8.9173E+00	8.9311E+00	1.0367E+01

FRANCK-CONDON FACTORS

V ₀	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27	V ₀₀ = 28
0	9.1107E-04	3.7310E-06	1.5036E-05	2.1087E-06
1	3.0770E-02	3.3030E-03	3.0482E-06	1.2390E-04
2	1.6958E-01	6.3504E-02	6.0690E-03	2.2059E-04
3	1.5490E-01	2.2112E-01	9.7981E-02	6.9479E-03
4	1.1578E-03	1.0619E-01	2.5545E-01	1.2543E-01
5	3.3421E-02	1.5571E-02	7.1896E-02	2.8268E-01

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27	V ₀₀ = 28
0	3.3154E+00	4.4175E+00	3.0792E+00	3.4168E+00
1	3.2149E+00	3.3458E+00	2.5268E-01	3.1606E+00
2	3.1635E+00	3.2279E+00	3.3889E+00	2.6723E+00
3	3.1403E+00	3.1760E+00	3.2430E+00	3.4617E+00
4	2.7006E+00	3.1682E+00	3.1910E+00	3.2608E+00
5	3.0378E+00	2.9535E+00	3.2116E+00	3.2085E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27	V ₀₀ = 28
0	1.0964E+01	1.8046E+01	9.4228E+00	1.1582E+01
1	1.0328E+01	1.1161E+01	-8.7657E+00	9.9480E+00
2	1.0007E+01	1.0413E+01	1.1440E+01	6.8139E+00
3	9.6673E+00	1.0088E+01	1.0512E+01	1.1913E+01
4	7.0496E+00	1.0048E+01	1.0186E+01	1.0628E+01
5	9.2258E+00	9.6748E+00	1.0330E+01	1.0301E+01

FRANCK-CONDON FACTORS

V ₀	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31	V ₀₀ = 32
0	1.8075E-07	9.7883E-08	1.0165E-08	3.0434E-09
1	5.9266E-06	4.0059E-06	2.9939E-07	2.9696E-07
2	4.6955E-04	5.6778E-07	2.6468E-05	6.0091E-08
3	1.6499E-03	1.0123E-03	4.9883E-05	7.1127E-05
4	4.0282E-03	6.2057E-03	1.1141E-03	5.3600E-04
5	1.3712E-01	1.4938E-04	1.4833E-02	2.0472E-04

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31	V ₀₀ = 32
0	2.7992E+00	3.3674E+00	2.8171E+00	3.5394E+00
1	3.6493E+00	3.0561E+00	3.6936E+00	3.1144E+00
2	3.2347E+00	6.3375E+00	3.2012E+00	4.1158E-01
3	2.9774E+00	3.3191E+00	2.6998E+00	3.3485E+00
4	3.6386E+00	3.1109E+00	3.4593E+00	3.0643E+00
5	3.2825E+00	5.7468E+00	3.1982E+00	4.1569E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31	V ₀₀ = 32
0	7.6104E+00	1.1245E+01	7.7144E+00	1.2327E+01
1	1.3078E+01	9.2605E+00	1.3339E+01	9.6205E+00
2	1.0427E+01	3.0355E+01	1.0198E+01	-7.7007E+00
3	8.7805E+00	1.0973E+01	6.9819E+00	1.1144E+01
4	1.3057E+01	9.6430E+00	1.1879E+01	9.3286E+00
5	1.0771E+01	2.6678E+01	1.0209E+01	1.6379E+01

Appendix 3b: Preliminary FCFs for $^{200}\text{Hg}^{79}\text{Br}$, $v' = 0-5$, $v'' = 12-31$.

FRANCK-CONDON FACTORS, R-CENTROIDS, AND R=2-CENTROIDS

INTEGRALS TAKEN OVER 241 POINTS, STARTING AT J = 1 FOR STATE 1 AND I = 141 FOR STATE 2

FRANCK-CONDON FACTORS

V_0	$V_{00} = 12$	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$
0	2.0793E-04	8.5923E-04	3.0493E-03	9.2809E-03
1	1.6028E-03	5.4907E-03	1.5657E-02	3.6694E-02
2	6.2299E-03	1.7477E-02	3.9195E-02	6.8010E-02
3	1.6131E-02	3.6367E-02	6.1929E-02	7.3915E-02
4	3.0947E-02	5.4475E-02	6.6247E-02	4.6287E-02
5	4.6227E-02	6.0623E-02	4.6624E-02	1.1432E-02

R-CENTROID VALUES (ANGSTROMS)

V_0	$V_{00} = 12$	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$
0	3.0543E+00	3.0675E+00	3.0813E+00	3.0958E+00
1	3.0429E+00	3.0554E+00	3.0683E+00	3.0816E+00
2	3.0320E+00	3.0439E+00	3.0560E+00	3.0684E+00
3	3.0217E+00	3.0329E+00	3.0443E+00	3.0557E+00
4	3.0117E+00	3.0224E+00	3.0331E+00	3.0432E+00
5	3.0022E+00	3.0123E+00	3.0220E+00	3.0289E+00

R=2-CENTROIDS

V_0	$V_{00} = 12$	$V_{00} = 13$	$V_{00} = 14$	$V_{00} = 15$
0	9.3305E+00	9.4115E+00	9.4961E+00	9.5851E+00
1	9.2606E+00	9.3366E+00	9.4155E+00	9.4974E+00
2	9.1944E+00	9.2662E+00	9.3399E+00	9.4155E+00
3	9.1314E+00	9.1993E+00	9.2683E+00	9.3374E+00
4	9.0712E+00	9.1354E+00	9.1995E+00	9.2603E+00
5	9.0134E+00	9.0738E+00	9.1318E+00	9.1715E+00

FRANCK-CONDON FACTORS

V_0	$V_{00} = 16$	$V_{00} = 17$	$V_{00} = 18$	$V_{00} = 19$
0	2.4134E-02	5.3302E-02	9.9093E-02	1.5308E-01
1	6.9144E-02	1.0080E-01	1.0543E-01	6.5691E-02
2	9.5833E-02	6.8687E-02	2.2201E-02	8.3146E-04
3	5.1782E-02	1.0582E-02	5.1134E-03	4.6391E-02
4	8.8082E-03	5.4079E-03	4.1602E-02	4.2069E-02
5	2.8606E-03	3.4406E-02	3.8204E-02	3.1148E-03

R-CENTROID VALUES (ANGSTROMS)

V_0	$V_{00} = 16$	$V_{00} = 17$	$V_{00} = 18$	$V_{00} = 19$
0	3.1109E+00	3.1270E+00	3.1461E+00	3.1625E+00
1	3.0954E+00	3.1097E+00	3.1240E+00	3.1374E+00
2	3.0809E+00	3.0931E+00	3.1021E+00	3.1016E+00
3	3.0666E+00	3.0728E+00	3.1119E+00	3.1134E+00
4	3.0490E+00	3.0618E+00	3.0938E+00	3.0937E+00
5	3.0601E+00	3.0605E+00	3.0686E+00	3.0629E+00

R=2-CENTROIDS

V_0	$V_{00} = 16$	$V_{00} = 17$	$V_{00} = 18$	$V_{00} = 19$
0	9.6791E+00	9.7700E+00	9.8637E+00	1.0002E+01
1	9.5824E+00	9.6703E+00	9.7594E+00	9.8419E+00
2	9.4920E+00	9.5644E+00	9.6199E+00	1.0140E+01
3	9.4032E+00	9.4378E+00	9.6899E+00	9.6946E+00
4	9.2928E+00	9.3029E+00	9.5182E+00	9.5698E+00
5	9.3706E+00	9.3674E+00	9.4157E+00	9.3722E+00

FRANK-CONDON FACTORS

V ₀	V ₀₀ = 20	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23
0	1.9310E+01	1.9396E+01	1.4953E+01	9.3538E+02
1	1.0781E+02	1.1159E+02	9.5429E+02	1.8543E+01
2	4.2214E+02	9.1327E+02	3.8764E+02	1.8979E+03
3	5.4735E+02	8.0618E+03	1.8565E+02	7.1179E+02
4	2.8559E+03	2.2560E+02	5.1677E+02	6.4304E+03
5	1.8901E+02	4.2133E+02	3.9765E+03	2.5110E+02

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 20	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23
0	3.1827E+00	3.2053E+00	3.2312E+00	3.2626E+00
1	3.1379E+00	3.2134E+00	3.2169E+00	3.2390E+00
2	3.1487E+00	3.1596E+00	3.1647E+00	3.3470E+00
3	3.1230E+00	3.1189E+00	3.1761E+00	3.1771E+00
4	3.0822E+00	3.1346E+00	3.1394E+00	3.1251E+00
5	3.1042E+00	3.1090E+00	3.0957E+00	3.1499E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 20	V ₀₀ = 21	V ₀₀ = 22	V ₀₀ = 23
0	1.0130E+01	1.0274E+01	1.0440E+01	1.0643E+01
1	9.8391E+00	1.0336E+01	1.0351E+01	1.0493E+01
2	9.9167E+00	9.9828E+00	1.0011E+01	1.1224E+01
3	9.7524E+00	9.7189E+00	1.0093E+01	1.0094E+01
4	9.4884E+00	9.8290E+00	9.8548E+00	9.7548E+00
5	9.6392E+00	9.6640E+00	9.5716E+00	9.9248E+00

FRANK-CONDON FACTORS

V ₀	V ₀₀ = 24	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27
0	3.0593E+02	5.9114E+03	2.7142E+04	3.1444E+05
1	1.8012E+01	9.3478E+02	2.1400E+02	7.0145E+04
2	1.0013E+01	2.1404E+01	1.6414E+01	4.2990E+02
3	2.4665E+02	2.4276E+02	1.9567E+01	2.2419E+01
4	2.8073E+02	5.5842E+02	4.7400E+04	1.6123E+01
5	3.9595E+02	4.1381E+04	4.8703E+02	3.3912E+03

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 24	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27
0	3.3041E+00	3.3708E+00	3.5754E+00	3.8196E+00
1	3.2689E+00	3.3102E+00	3.3807E+00	3.6658E+00
2	3.2553E+00	3.2781E+00	3.3178E+00	3.3927E+00
3	3.1607E+00	3.3071E+00	3.2923E+00	3.3273E+00
4	3.1883E+00	3.1769E+00	3.9734E+00	3.3141E+00
5	3.1504E+00	3.3046E+00	3.1760E+00	2.8642E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 24	V ₀₀ = 25	V ₀₀ = 26	V ₀₀ = 27
0	1.0913E+01	1.1357E+01	1.2711E+01	8.9934E+00
1	1.0486E+01	1.0955E+01	1.1419E+01	1.3317E+01
2	1.0602E+01	1.0748E+01	1.1007E+01	1.1501E+01
3	9.9777E+00	1.0949E+01	1.0844E+01	1.1072E+01
4	1.0168E+01	1.0086E+01	1.5399E+01	1.0991E+01
5	9.9231E+00	1.0918E+01	1.0081E+01	7.9910E+00

FRANCK-CONDON FACTORS

V ₀	V ₀₀ = 28	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31
0	2.7046E-05	5.2762E-09	1.1815E-06	6.8061E-09
1	3.4443E-04	1.4691E-04	3.4876E-06	9.9009E-06
2	6.0248E-04	1.7319E-03	3.2365E-04	7.9915E-05
3	6.2595E-02	4.8743E-06	5.4150E-03	2.3767E-04
4	2.7008E-01	7.0811E-02	2.2555E-03	1.1303E-02
5	1.3745E-01	3.0357E-01	5.9644E-02	1.5907E-02

R-CENTROID VALUES (ANGSTROMS)

V ₀	V ₀₀ = 28	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31
0	3.3641E+00	5.4064E+00	3.2979E+00	4.8147E+00
1	3.1547E+00	3.4254E+00	2.6820E+00	3.3968E+00
2	3.9124E+00	3.2404E+00	3.5192E+00	3.1275E+00
3	3.4081E+00	1.1923E+01	3.3052E+00	3.7727E+00
4	3.3389E+00	3.4292E+00	2.8853E+00	3.3837E+00
5	3.3440E+00	3.3522E+00	3.4617E+00	3.1833E+00

R=2-CENTROIDS

V ₀	V ₀₀ = 28	V ₀₀ = 29	V ₀₀ = 30	V ₀₀ = 31
0	1.1286E+01	2.4888E+01	1.0800E+01	2.0919E+01
1	9.8866E+00	1.1698E+01	6.7350E+00	1.1494E+01
2	1.4968E+01	1.0470E+01	1.2326E+01	9.7867E+00
3	1.1608E+01	6.8542E+01	1.0906E+01	1.4021E+01
4	1.1151E+01	1.1750E+01	8.1042E+00	1.1299E+01
5	1.1193E+01	1.1242E+01	1.1970E+01	1.0100E+01